Supporting Information

Precise Synthesis of Bottlebrush Block Copolymers from ω-End-Norbornyl Polystyrene and Poly(4-*tert*-butoxystyrene) via Living Anionic Polymerization and Ring-Opening Metathesis Polymerization

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Contents

1. ^{1}H and ^{13}C NMR spectra of chemical compounds

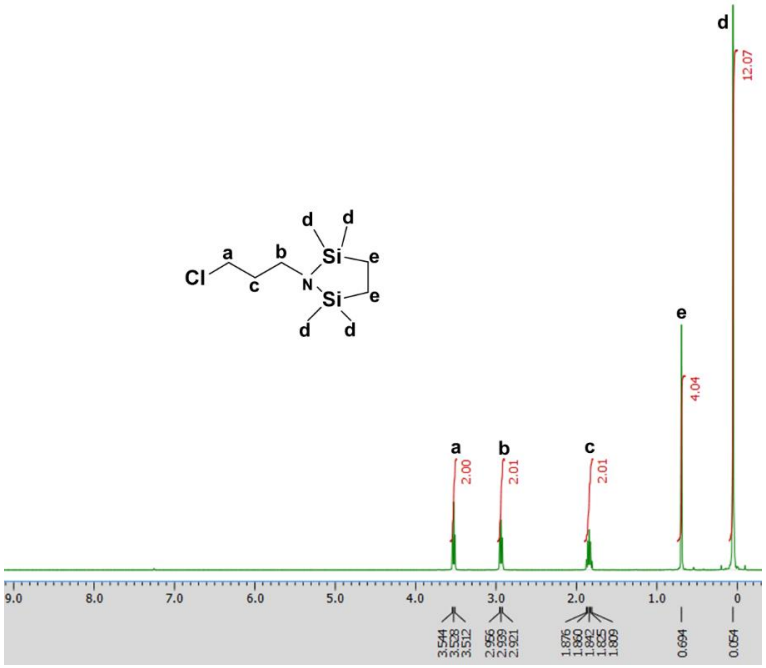

Figure S1. ^{1}H NMR spectrum of 2,2,5,5-tetramethyl-1-(3-chloropropyl)-1-aza-2,5-disilacyclopentane (T1) in $CDCl_3$ (400 MHz).

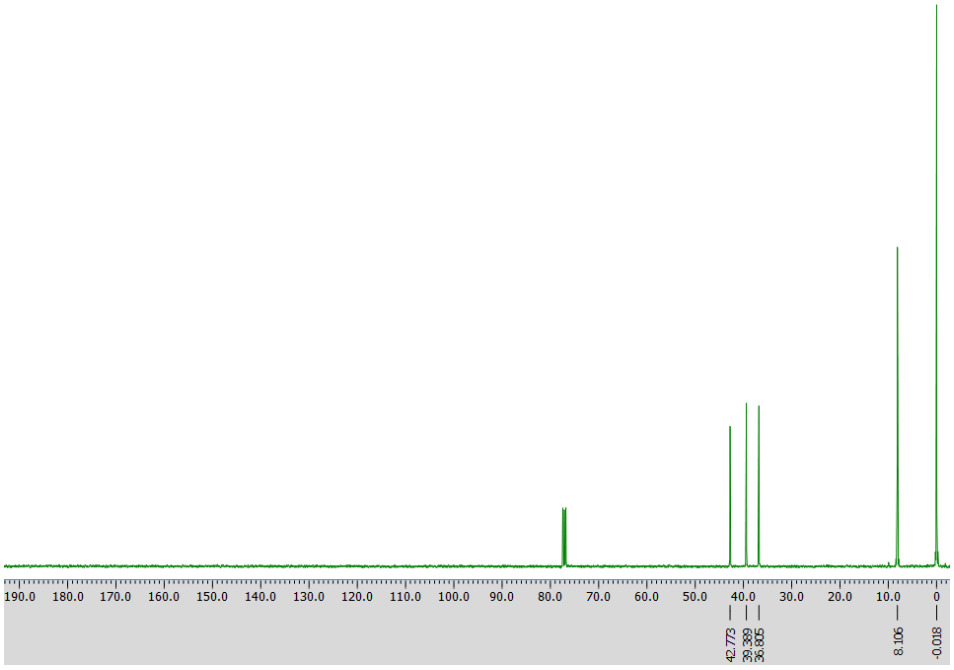

Figure S2. ^{13}C NMR spectrum of 2,2,5,5-tetramethyl-1-(3-chloropropyl)-1-aza-2,5-disilacyclopentane (T1) in $CDCl_3$ (100 MHz).

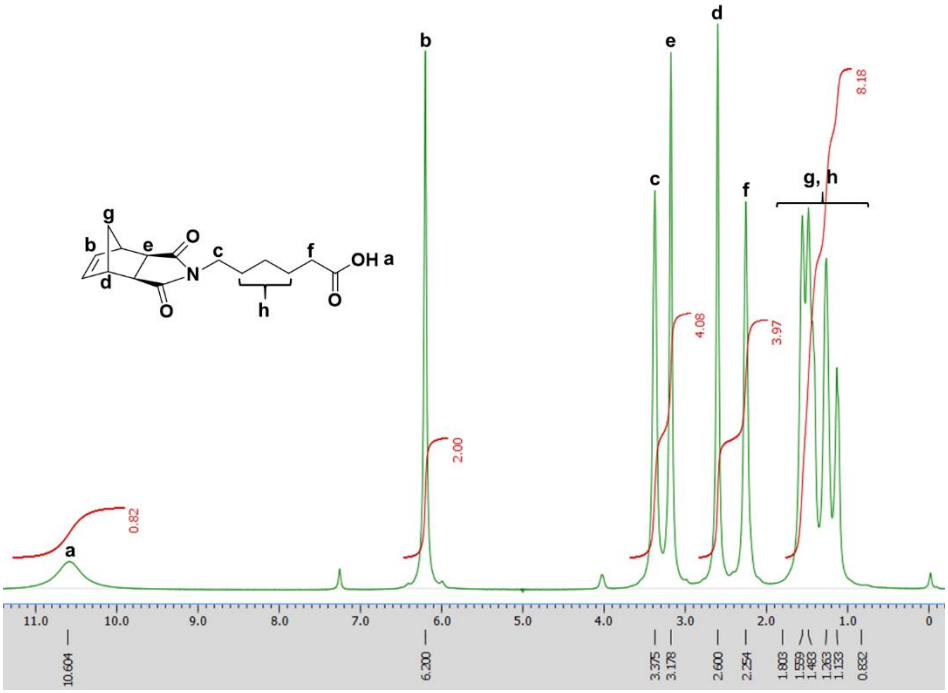

Figure S3. ^{1}H NMR spectrum of *N*-(carboxylhexanoyl)-*cis*-norbornene-exo-2,3-dicarboxiimide in $CDCl_3$ (400 MHz).

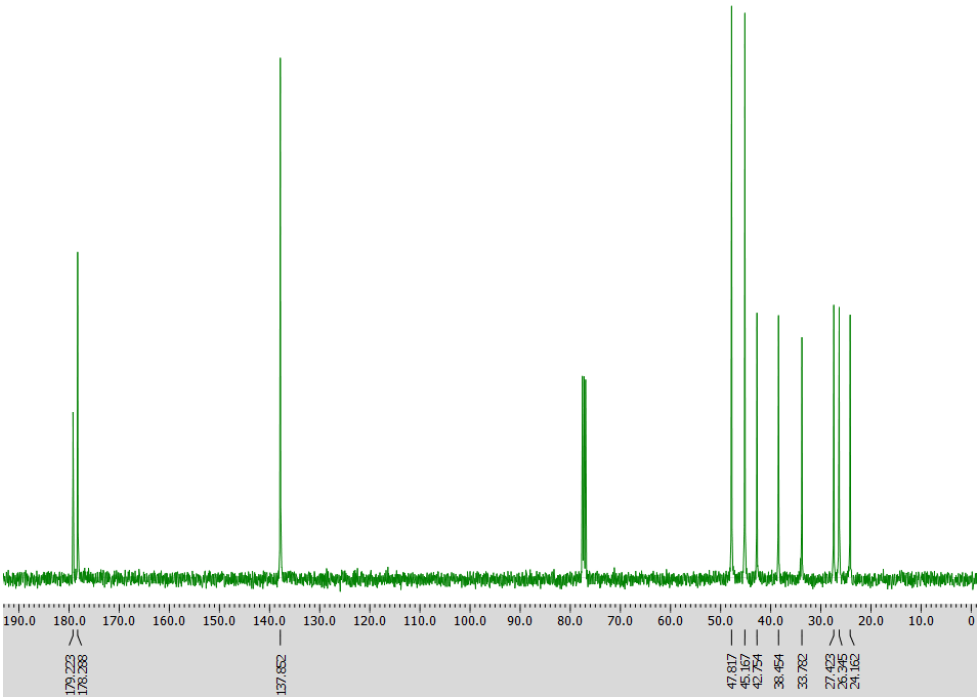

Figure S4. ^{13}C NMR spectrum of *N*-(carboxylhexanoyl)-*cis*-norbornene-exo-2,3-dicarboxiimide in $CDCl_3$ (100 MHz).

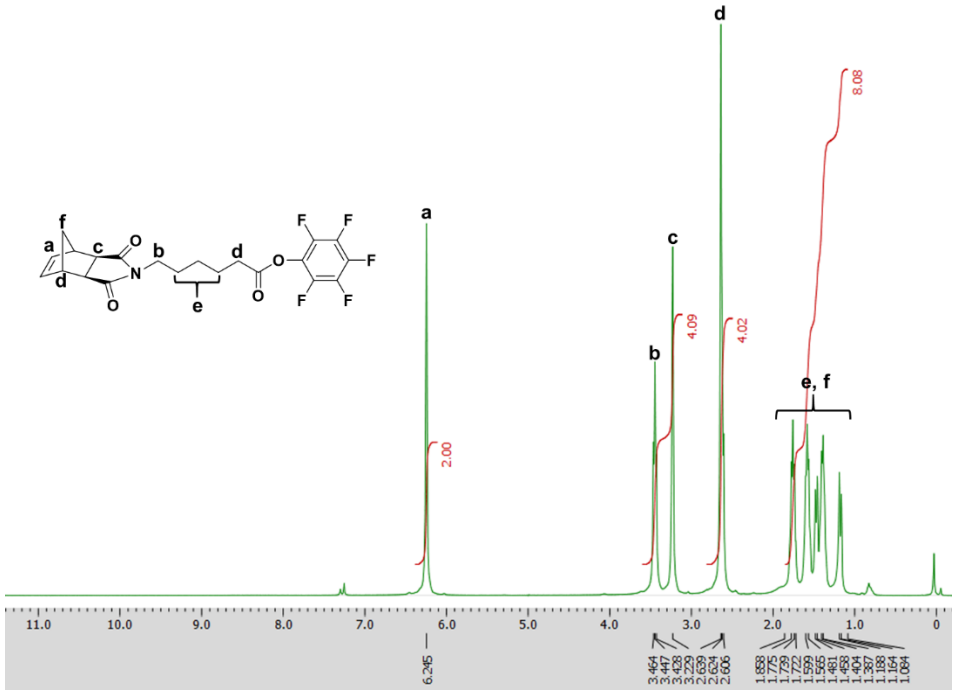

Figure S5. ^{1}H NMR spectrum of *N*-(perfluorophenyl hexanoate)-*cis*-norbornene-exo-2,3-dicarboxiimide (T2) in $CDCl_3$ (400 MHz).

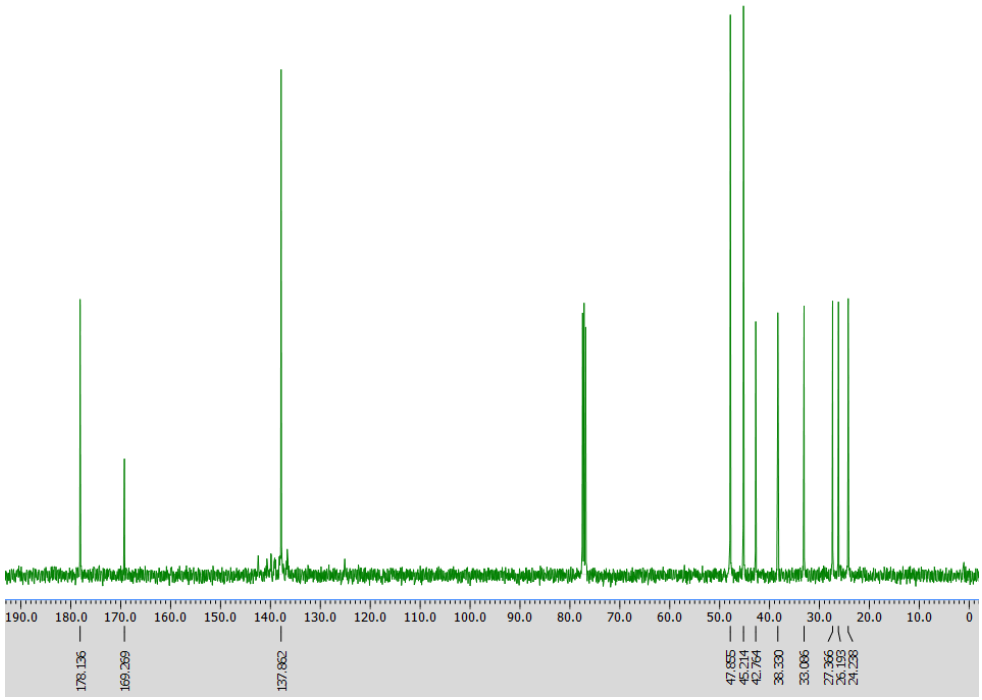

Figure S6. ^{13}C NMR spectrum of *N*-(perfluorophenyl hexanoate)-*cis*-norbornene-exo-2,3-dicarboxiimide (T2) in $CDCl_3$ (100 MHz).

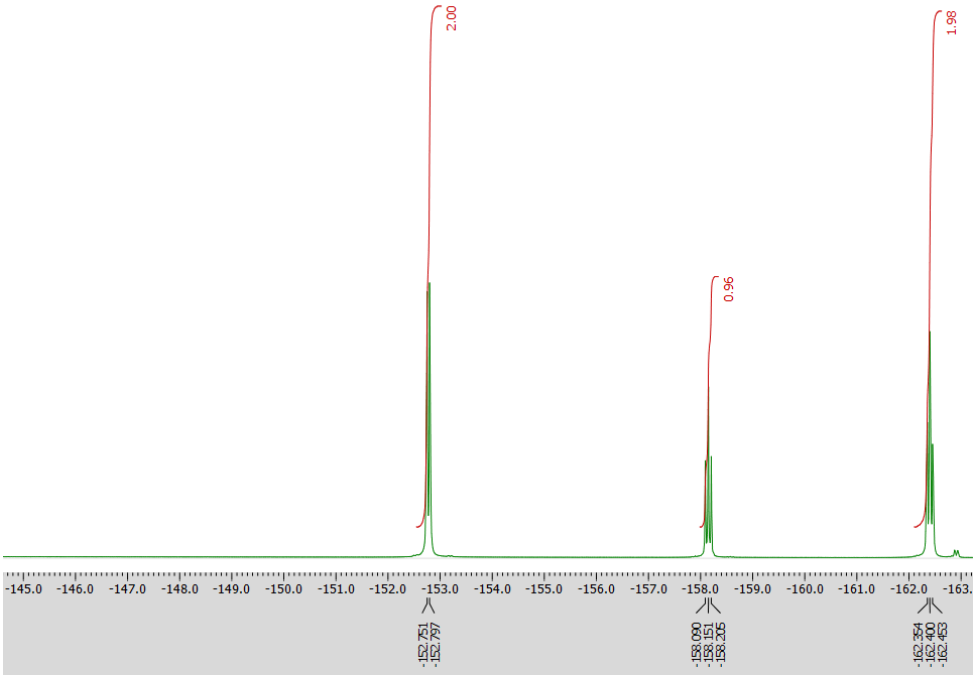

Figure S7. ^{9}F NMR spectrum of *N*-(perfluorophenyl hexanoate)-*cis*-norbornene-exo-2,3-dicarboxiimide (T2) in $CDCl_3$ (376 MHz).

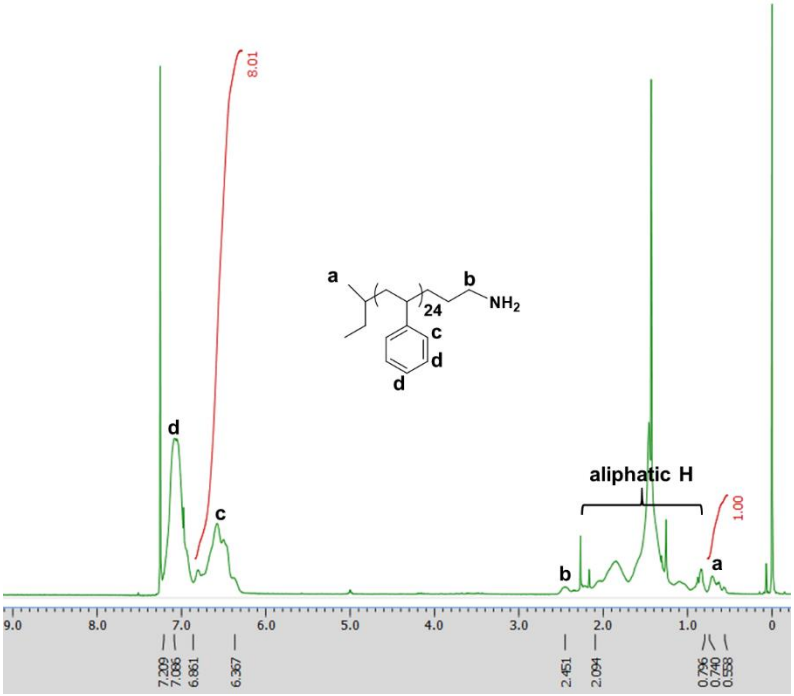

Figure S8. ^{1}H NMR spectrum of PSt-NH_2 in $CDCl_3$ (400 MHz).

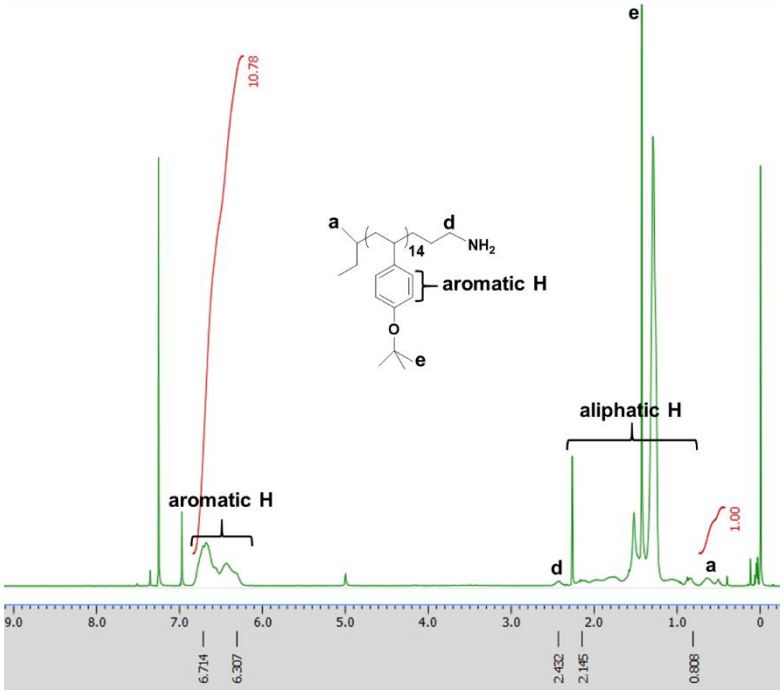

Figure S9. ^{1}H NMR spectrum of P*t*BOS-NH_2 in $CDCl_3$ (400 MHz).

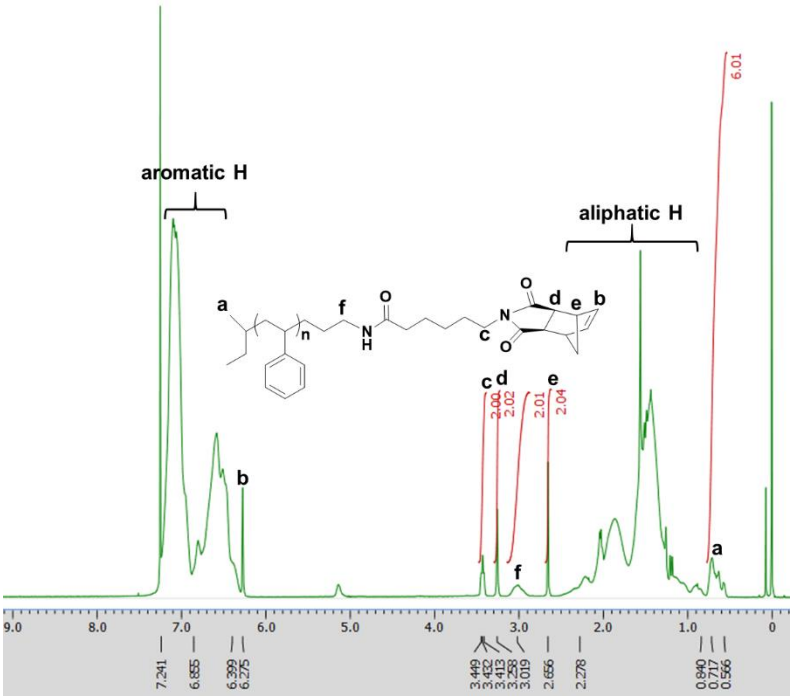

Figure S10. ^{1}H NMR spectrum of NPSt in $CDCl_3$ (400 MHz).

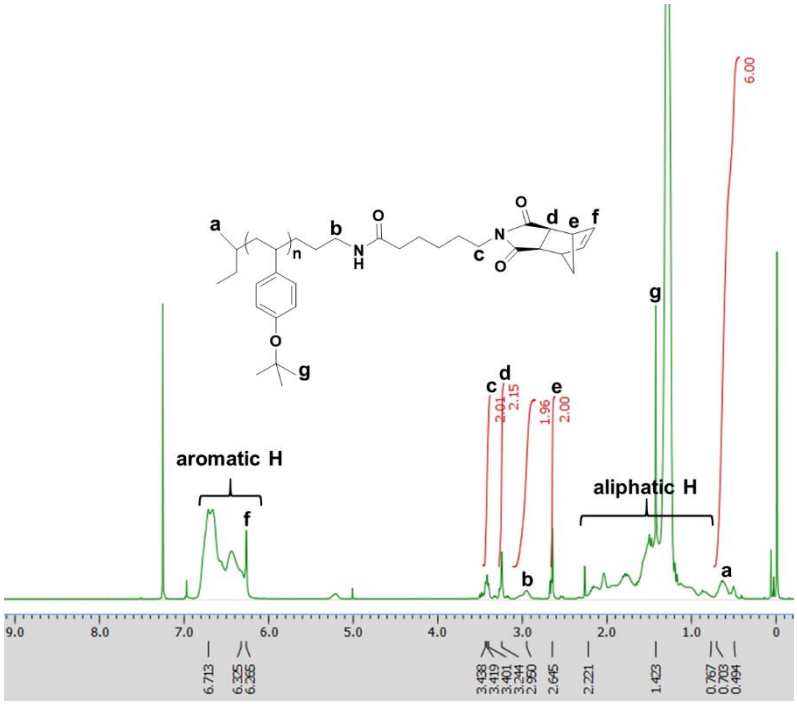

Figure S11. ^{1}H NMR spectrum of NP*t*BOS in $CDCl_3$ (400 MHz).

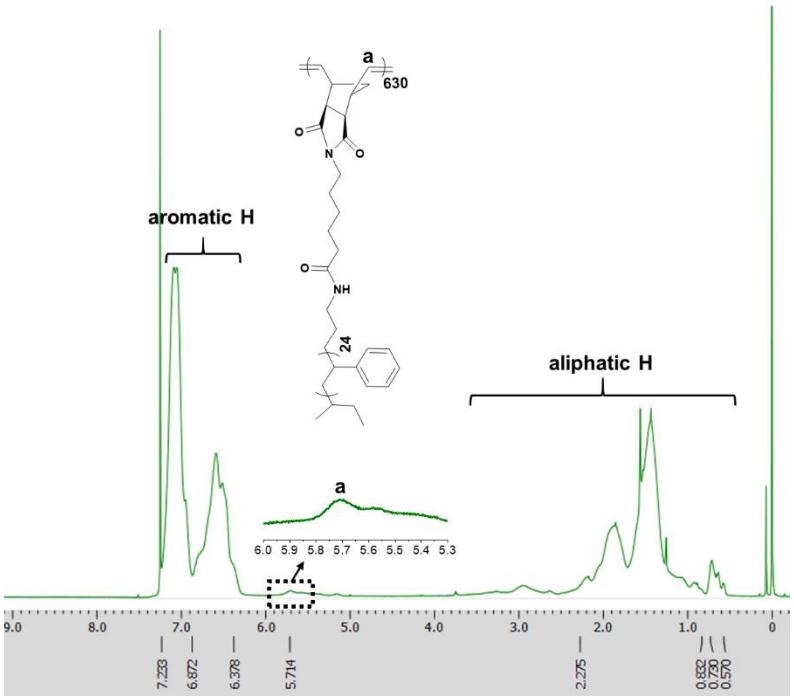

Figure S12. ^{1}H NMR spectrum of P(NB-*g*-St)$_{630}$ in $CDCl_3$ (400 MHz).

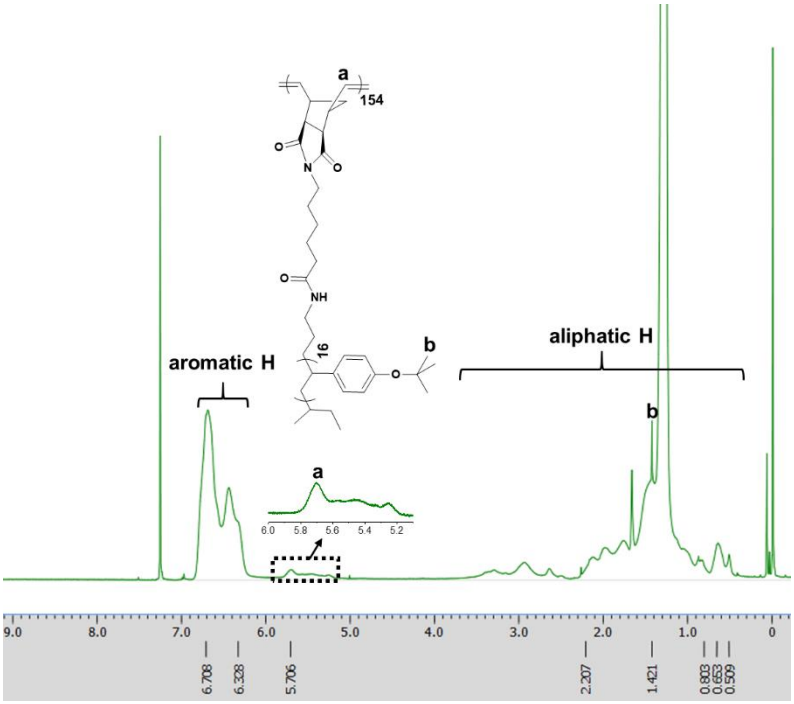

Figure S13. ^{1}H NMR spectrum of P(NB-*g*-*t*BOS)$_{154}$ in $CDCl_3$ (400 MHz).

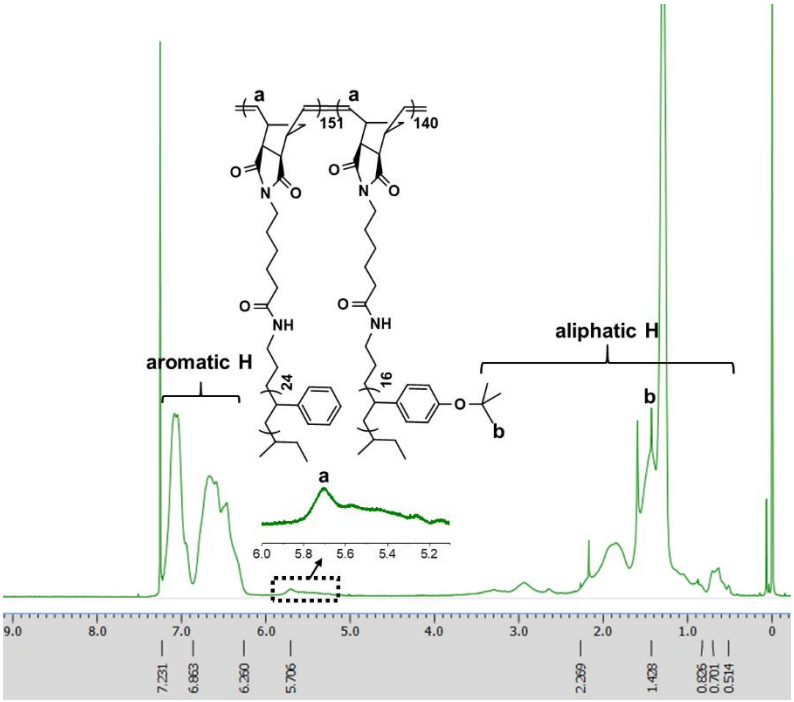

Figure S14. ^{1}H NMR spectrum of P(NB-*g*-St)$_{151}$-*b*-P(NB-*g*-*t*BOS)$_{140}$ in $CDCl_3$ (400 MHz).

2. Physical data of macromonomers

Table S1. Characteristics of *ω*-norbornyl macromonomers

entry	MM	$M_{n,NMR}$ (kDa)	$M_{n,obsd}$[a] (kDa)	$Đ$[a]	DP_n
1	NPSt	2.76	2.69	1.14	24
2	NPSt	3.23	3.37	1.07	28
3	NP*t*BOS	2.79	2.43	1.06	14
4	NP*t*BOS	3.13	3.01	1.06	16

[a]$M_{n,obsd}$ and $Đ$ were obtained by SEC calibration using polystyrene standard in THF containing 2% trimethylamine as the eluents at 40 ℃.

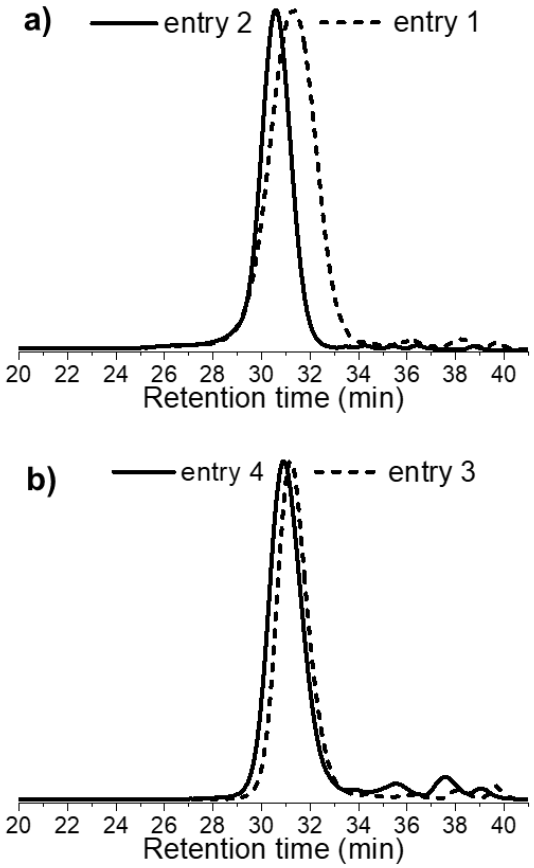

Figure S15. GPC curves of the macromonomers of (a) NPSt and (b) NP*t*BOS

3. Additional SEM images and photographs of films of Bottlebrush block copolymers

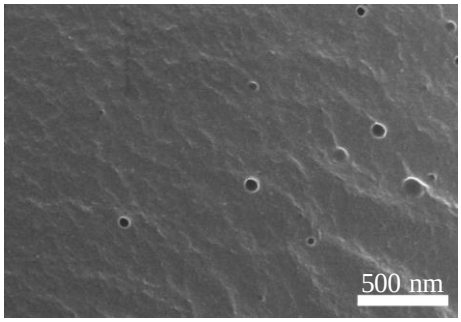

Figure S15. Cross-sectional SEM image of P(NB-*g*-St)-*b*-P(NB-*g*-*t*BOS) with M_w = 148 kDa and DP_w = 52 (Table 2, entry 1).

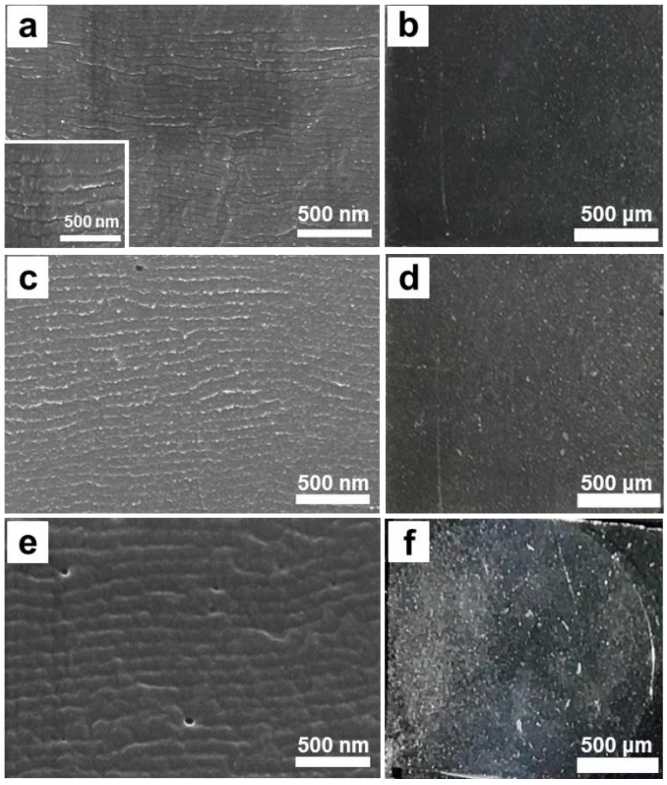

Figure S16. Cross-sectional SEM images and photographs of photonic films of P(NB-*g*-St)-*b*-P(NB-*g*-*t*BOS) with (a,b) M_w = 296 kDa (Table 2, entry 2), (c,d) M_w = 830 kDa (Table 2, entry 3), and (e,f) M_w = 1331 kDa (Table 2, entry 4).

4. Additional kinetic profile on ROMP of NPSt in THF at room temperature ($[NPSt]_0 = 0.05$ M)

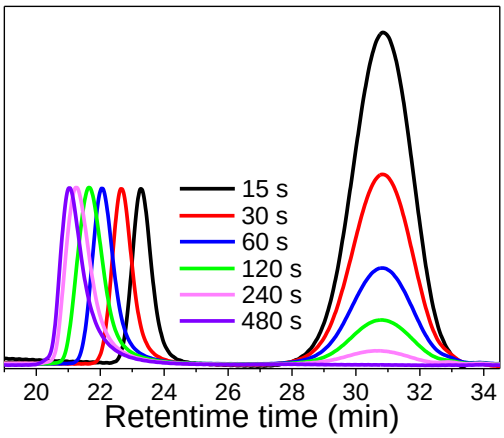

Figure S17. SEC traces of P(NB-*g*-St) aliquots with $[NPSt]_0/[G3]_0 = 650$ withdrawn from mixture during ROMP at time intervals (Table1, entry 3).